

SCIENCE FOR GLASS PRODUCTION

UDC 666.192:541.183:537.363.001.5

EVALUATION OF ELECTRICAL SURFACE PROPERTIES OF HYDRATED QUARTZ-GLASS PARTICLES BASED ON THE ζ -POTENTIAL VALUE

Yu. K. Shchipalov¹Translated from *Steklo i Keramika*, No. 11, pp. 3 – 6, November, 1999.

Based on the results of measuring the ζ -potential of quartz-glass hydrated particles, an estimate of the number of mechanically and thermally ruptured Si – O – Si bonds per surface-area unit of quartz glass, which is the source of the electrical surface properties of the particles, is given.

The electrical surface properties of hydrated glass particles are determined by the quantity of silanol groups $\equiv \text{Si} - \text{OH}$ per glass surface unit. These groups are capable of dissociation accompanied by release of H^+ protons or ionic exchange with other ambient medium cations, which is important in glass-filter service.

The present paper describes an attempt to evaluate the number of $\equiv \text{Si} - \text{OH}$ groups on the surface of vitreous silica based on the results of measuring the electrokinetic potential of quartz-glass hydrated particles.

The tested materials were optically pure quartz glass and pure piezoquartz (β -quartz) obtained by the hydrothermal method. The weight content of impurity cations in these materials is below $10^{-4} \%$, which is evidence of their high degree of purity.

Quartz glass and β -quartz were pulverized in an agate mortar to a particle size of $1 - 30 \mu\text{m}$. Powder samples were placed in clean quartz test tubes, and bidistilled water was poured over them, after which the samples were held in water for 0.1, 0.5, 1, 1.5, and 2 h, as well as 1, 2, 3, 4, and 5 days. In order to diminish the effect of even those insignificant quantities of impurity cations which are contained in the quartz test tubes, piezoquartz, and quartz glass, each day the liquid was decanted from the test tubes, which were then filled with fresh portions of bidistilled water. Before measuring the ζ -potential, the test tubes with their content were shaken, and then the suspension was left to settle for 1 – 2 min (to allow sedimentation of larger particles). Next, suspension samples were placed in an electrophoretic chamber using a

syringe. In this particular case, the amplitude-frequency method of microelectrophoresis [1] was used to determine the ζ -potential of hydrated particles of quartz glass and β -quartz, since this method ensures high accuracy (95 – 97%) and gives stable values of the ζ -potential. The measured parameter in the experiments was the vibration amplitude of hydrated particles in an alternating bipolar field of 10-V voltage and 0.25-Hz frequency. The amplitude values were used to calculate the electrophoretic velocity of solid-particle migration in the dispersion medium (water), and this velocity value was then substituted into the classical Smolukhovskii formula to calculate the ζ -potential [1].

Figure 1 shows the results of the study. As can be seen, the values of the ζ -potential sharply increase in the first

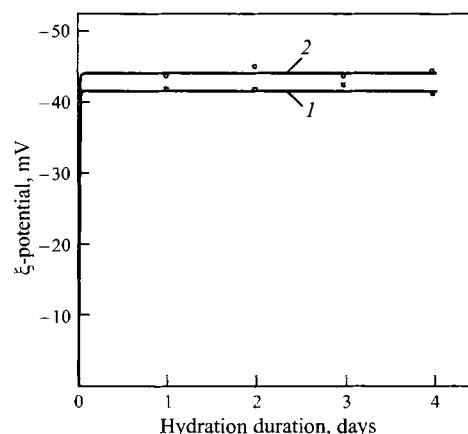


Fig. 1. Dependence of the ζ -potential on hydration duration: 1) quartz; 2) quartz glass.

¹ Ivanovo State Chemical Engineering University, Ivanovo, Russia.

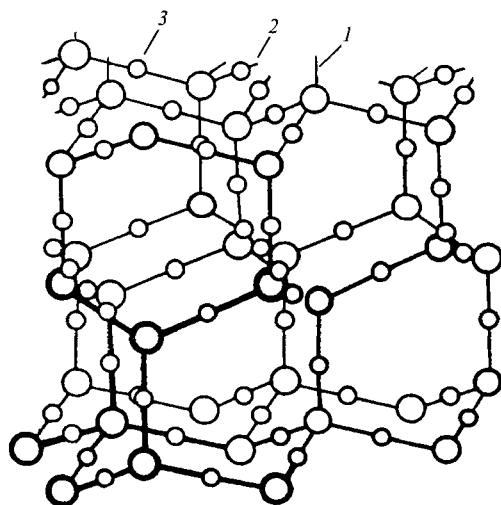
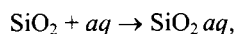


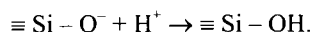
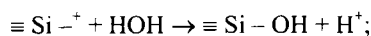
Fig. 2. Structure of silica surface: 1) Si atoms; 2) O atoms; 3) O bridge atoms.

1.5 – 2 h of contact of the particles with water and then become virtually stable and constitute – 42 mV for quartz particles and – 45 mV for quartz glass particles.

The fracture surface in the particles produced by dispersion of β -quartz and quartz glass has a conchoidal relief, due to the helical joining of $[\text{SiO}_4]$ tetrahedrons in their structures. This fracture surface contains broken bonds (Fig. 2) both of the silicated type $\equiv \text{Si} - ^+ 1$ and the oxylated type $\equiv \text{Si} - \text{O}^- 2$, which is necessary for satisfying the condition of electric neutrality for the surface of silica particles. However, some part of the oxygen bridge atoms 3 which have no ruptured bonds and, therefore, are incapable of exhibiting surface electrical activity are also located on the fracture surface. Such capacity for surface electrical activity is exhibited only by particles of types 1 and 2. These are the activity centers in which, first, the absorption of water molecules (hydration) takes place:



and then their splitting (hydrolysis) occurs in the specified nodes according to the scheme



Consequently, not all Si and O nodes located on the fracture surface of quartz and quartz glass are subjected to hydration and hydrolysis when these particles are mixed with water.

The simplest way of estimating the quantity of all surface nodes n' and the quantity of nodes with broken bonds n per surface area unit of a solid particle is to analyze the cristobalite lattice, which has a cubic structure ($a = 0.716$ nm). The total number of surface nodes per nm^2 of cristobalite surface for {100} and {111} lattices is about 8, and the number of nodes with broken bonds is around 5. These calculations

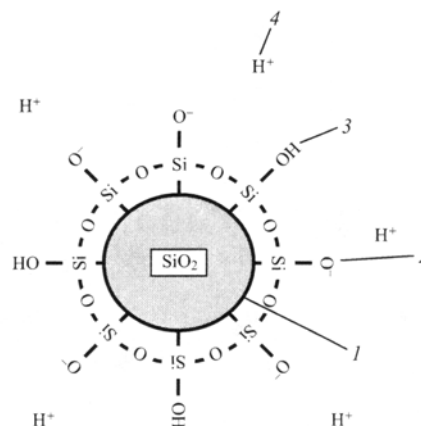


Fig. 3. Structural diagram of a hydrated quartz-glass particle: 1) nucleus; 2) potential-determining ions; 3) adsorption-layer counterions; 4) diffusion-layer counterions.

agree with the published data [2], which indicate $n'_{\text{cryst}} = 7.8$ nodes and $n_{\text{cryst}} = 4.6$ nodes per nm^2 . The latter value is accepted by us as the most reliable one for further reasoning.

Knowing the densities of β -quartz (2.65 g/cm^3), quartz glass (2.21), and cristobalite (2.32), it is possible to estimate the number of mechanically ruptured bonds per surface-area unit (1 nm^2) in the first two substances:

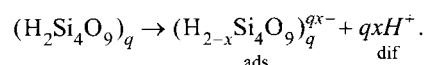
$$n_{\beta-q} = \frac{n_{\text{cryst}}}{(\rho_{\text{cryst}} / \rho_{\beta-q})^{2/3}} = \frac{4.6}{(0.875)^{2/3}} = 5.02; \quad (1)$$

$$n_{q.g.} = \frac{n_{\text{cryst}}}{(\rho_{\text{cryst}} / \rho_{q.g.})^{2/3}} = \frac{4.6}{(1.05)^{2/3}} = 4.47. \quad (2)$$

It is evident that the values of n_{cryst} , $n_{\beta-q}$, and $n_{q.g.}$ also correlate with the number of silanol groups $\equiv \text{Si} - \text{OH}$ that have been formed per surface-area unit of hydrated forms of these varieties of silica.

The hydrated surface in all cases is a continuous film of polysilicic acid $(\text{H}_2\text{Si}_4\text{O}_9)_q$ which envelops the siliceous nucleus of the hydrated particle (micelle) and is bonded to the nucleus by the siloxane bond $\text{Si} - \text{O}$, whereas the OH groups are oriented toward the dispersion medium, i.e., water (Fig. 3).

Such polysilicic acid always dissociates to some extent, emitting H^+ protons into the ambient medium. The remaining silanol groups $\equiv \text{Si} - \text{O}^-$ develop a potential-determining micelle layer, the protons existing in the remaining nondissociated silanol groups $\equiv \text{Si} - \text{OH}$ create the adsorption layer of counterions, and all H^+ protons that have left the micelle surface make up part of the counterion diffusion layer:



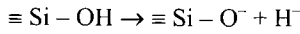
The negative charge qx is the source of the surface potential of β -quartz and quartz-glass particles at the level of the

counterion adsorption layer φ_a , and part of this potential is the ζ -potential of these particles at the gliding boundary, which is located at a distance r from the surface of the solid particles:

$$\xi = \varphi_a e^{-\aleph r}, \quad (3)$$

where \aleph is a constant, whereas $1/\aleph$ is equal to the effective thickness of the diffusion segment of the micelle double electric layer [3].

According to researchers, the number of $\equiv \text{Si} - \text{OH}$ groups capable of ionization in polysilicic acids is equal to 2.43 groups per nm^2 of surface area [2], i.e., the dissociation degree k of the process



for hydrated surface of cristobalite is equal to

$$k = \frac{[\text{H}^+]}{[\equiv \text{Si} - \text{OH}]} = \frac{2.43}{4.6} = 0.53.$$

The dissociation constant of this process

$$K_d = \frac{[\equiv \text{Si} - \text{O}^-][\text{H}^+]}{[\equiv \text{Si} - \text{OH}]}$$

is around $10^{-6.5} - 10^{-7.2}$ [2].

If we accept the dissociation degree of silanol groups (0.53) to be constant for all hydrated silica forms (including β -quartz and quartz glass), then the electric charge density σ per surface-area unit of these materials will be

$$\sigma_{\beta-q} = n_{\beta-q} \times 0.53e = 5.02 \times 0.53 \times 1.6 \times 10^{-19} = 4.256 \times 10^{-19} \text{ C/nm}^2,$$

$$\sigma_{q.g.} = n_{q.g.} \times 0.53e = 4.47 \times 0.53 \times 1.6 \times 10^{-19} = 3.792 \times 10^{-19} \text{ C/nm}^2,$$

where $e = 1.6 \times 10^{-19} \text{ C}$ is the charge of the electron.

The same values, but taken with the “+” sign, correspond to the total proton charges in the micelle diffusion layers (per surface-area unit of solid particles). It is arbitrarily assumed in this case that there are only mechanically ruptured chemical bonds on the surface of β -quartz and quartz-glass particles. In this case, $n_{\beta-q} > n_{q.g.}$ and $\sigma_{\beta-q} > \sigma_{q.g.}$.

However, the measurements of the ζ -potential show that the surface electrical activity of quartz-glass hydrated particles is higher than that of β -quartz.

The ζ -potential (the potential at the gliding boundary between micelle and water) is part of the adsorption potential φ_a (i.e., the potential at the boundary between the adsorption and diffusion counterion layers). For a solid spheroid particle with radius R and charge surface density σ (provided that the

size of the protons in the counterion adsorption layer can be neglected), this potential is equal to [4]:

$$\varphi_a = \frac{q}{4\pi\epsilon\epsilon_0 R} = \frac{4\pi R\sigma}{4\pi\epsilon\epsilon_0 R} = \frac{\sigma R}{\epsilon\epsilon_0},$$

where ϵ is the relative dielectric constant of water (81) and ϵ_0 is the electric constant ($8.854 \times 10^{-12} \text{ F/m}$).

Then

$$\varphi_a^{q.g.} = \frac{\sigma_{q.g.} R}{\epsilon\epsilon_0}; \quad \varphi_a^{\beta-q} = \frac{\sigma_{\beta-q} R}{\epsilon\epsilon_0}$$

and, accordingly (based on Eq. (3)),

$$\xi_{q.g.} = \frac{\sigma_{q.g.} R}{\epsilon\epsilon_0} e^{-\aleph_1 r_1}; \quad \xi_{\beta-q} = \frac{\sigma_{\beta-q} R}{\epsilon\epsilon_0} e^{-\aleph_2 r_2}.$$

Neither \aleph_1 and \aleph_2 nor r_1 and r_2 are known in these equations, but it can be assumed that analogous values for two hydrated forms of silica hardly differ significantly.

Dividing one equation by the other, we get

$$\xi_{q.g.}/\xi_{\beta-q} \approx \sigma_{q.g.}/\sigma_{\beta-q} \approx n_{q.g.}/n_{\beta-q}, \quad (4)$$

which contradicts the theoretical reasoning (Eqs. (1) and (2)). This contradiction is easily removed if we take into account that quartz glass is thermodynamically a less stable phase than β -quartz, since the former is a “frozen” melt of SiO_2 . In melting SiO_2 , many $\text{Si} - \text{O}$ bonds are thermally ruptured, which accounts for the decrease in the melt viscosity. When SiO_2 is rapidly chilled (“frozen”), a substantial part of these bonds do not have enough time to heal, and some sp^3 -orbitals of Si particles and p -orbitals of O particles are not overlapped by each other.

Thus, in addition to the $\text{Si} - \text{O} - \text{Si}$ bonds mechanically broken in dispersion, the quartz-glass particles also have a certain amount of thermally broken bonds (inherited from the melt).

It follows from Eq. (4) that the true charge density on the surface of hydrated quartz glass is

$$\sigma_{q.g.}^{\text{true}} = \sigma_{\beta-q} \frac{\xi_{q.g.}}{\xi_{\beta-q}},$$

and the quantity of all ruptured bonds on the surface of freshly fractured quartz glass per surface-area unit (1 nm^2) is equal to

$$n_{q.g.}^{\text{true}} = n_{\beta-q} \frac{\xi_{q.g.}}{\xi_{\beta-q}} = 5.02 \frac{(-45)}{(-42)} = 537.$$

Of the above quantity, 4.47 corresponds to mechanically broken bonds (formed in pulverizing) and 0.9 corresponds to thermally broken bonds (inherited from the melt).

These results are obtained based on the assumption that the degree of dissociation of $\equiv \text{Si} - \text{OH}$ groups is constant for all hydrated forms of silica ($k = 0.53$), and the thickness of the gliding layer r and the diffusion layer of counterions $1/\kappa$ is similar in all cases.

Obviously, a certain discrepancy in these values does occur. An increase in the number of silanol groups $\equiv \text{Si} - \text{OH}$ per surface-area unit in quartz glass (5.37) compared to this value for β -quartz (5.02), even with the same dissociation degree (0.53), produces variations in the number of protons in the micelle diffusion layer per nm^2 (2.85 and 2.66, respectively). Considering that the number of protons remaining in $\equiv \text{Si} - \text{OH}$ groups located on the particle surface is higher in the former case as well (2.52 and 2.36, respectively), one can expect increased repulsion of these protons in the adsorption layer and transition of their additional quantity into water (i.e., $k_{\text{q.g.}} \neq k_{\beta\text{-q}}$).

In that case, the gliding-layer thickness (and the diffusion-layer thickness) in quartz-glass particles should be higher than that of β -quartz particles. Indeed, the equilibrium distance L between the protons experiencing mutual repulsion within the gliding-volume limits can be considered constant in both cases. Hence, the gliding volume V_{gl} per surface-area unit of solid particles will be equal to approximately $n_{\text{gl}} L^3$ (n_{gl} is the number of protons in the gliding layer). Taking into account the above, it is obvious that $V_{\text{q.g.}}^{\text{gl}} > V_{\beta\text{-q}}^{\text{gl}}$.

However, all the specified shortcomings do not disturb the fundamental approach to the problem considered, since $\zeta_{\text{q.g.}}/\zeta_{\beta\text{-q}} = 1.07$, that is, this value is low.

The microcracks existing in the surface and near-surface layers of solid quartz glass and β -quartz particles do not disprove our reasoning, since these microcracks increase the surface area of contact between the particles and the water and contribute to the actual values of the experimentally measured ζ -potential. The average ratio between the mechanically and thermally broken bonds in microcracks is probably the same as in the surface nodes.

Thus, the determination of the ζ -potential in hydrated quartz-glass particles makes it possible to evaluate not only their electrophoretic activity, which is significant for molding by electrophoresis, but also the number of surface defects on these particles by distinguishing the amount of mechanically and thermally ruptured bonds. This is essential in analysis of surface electrical activity of quartz-glass particles in suspensions, as well as in accounting for sintering processes in the production of articles based on quartz-glass powders.

REFERENCES

1. Yu. K. Shchipalov, S. E. Tumanova, and K. K. Smirnov, "Dependence of the electrokinetic potential of vitreous substances on the duration of their surface hydration," *Steklo Keram.*, No. 4, 7–10 (1997).
2. R. Iler, *Chemistry of Silica*, Wiley, New York (1979).
3. A. Adamson, *The Physical Chemistry of Surfaces*, Wiley, New York (1976).
4. B. M. Yavorskii and Yu. A. Seleznev, *Reference Manual in Physics* [in Russian], Fizmatlit, Moscow (1989).